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THERMAL PROPERTIES OF DOPED AMMONIUM NITRATE.

PART 1. EVALUATION USING ACCELERATING RATE CALORIMETRY

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P.P. Lee* and R.R. Vandebeek**

ABSTRACT

The thermal stability of three ammonium nitrate (AN) samples, KNO_3 doped, NiO doped and CuO doped, were evaluated using an accelerating rate calorimeter and they were compared to A.C.S. grade AN. The onset decomposition temperature of NiO doped AN was detected at 235°C which indicates higher stability than KNO_3 doped AN and CuO doped AN. KNO_3 doped AN sample produces more residue after ignition, approximately 14%.

KEYWORDS: ammonium nitrate, potassium nitrate, nickel oxide, copper oxide, thermal stability, accelerating rate calorimetry.

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PROPRIÉTÉS THERMIQUES DU NITRATE D'AMMONIAQUE DOPÉ PARTIE 1. ÉVALUATION D'ÉCHANTILLONS DE NITRATE D'AMMONIAQUE AU MOYEN DE LA CALORIMÉTRIE À VITESSE ACCÉLÉRÉE

P.P. Lee* et R.R. Vandebeek**

RÉSUMÉ

La stabilité thermique de trois échantillons de nitrate d'ammoniaque (NA) additionnés de KNO_3, de NiO et de CuO a été évaluée au moyen d'un calorimètre à vitess accélérée, et comparée à celle du nitrate d'ammoniaque de qualité A.C.S. Au départ, la température de décomposition du nitrate d'ammoniaque additionné de NiO était de 235°C, ce qui indique une stabilité plus élevée que la température de décomposition de l'échantillon de nitrate d'ammoniaque additionné de KNO_3 et que celle de l'échantillon additionné de CuO. L'échantillon de nitrate d'ammoniaque additionné de KNO_3 est celui qui a produit la plus grande quantité de résidus après l'inflammation, soit environ 14%.

MOTS CLÉS: nitrate d'ammoniaque, nitrate de potassium, oxyde de nickel, oxyde de cuivre, stabilité thermique, calorimétrie à vitesse accélérée.

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INTRODUCTION

Ammonium nitrate (AN) is attractive for use in propellants and explosives because it can be obtained technically in a very pure state, it is chemically stable and it has low sensitivity to friction and shock. The restrictions to use are its hygroscopic property and its five polymorphic forms. At atmospheric pressure it can exist in five modifications from below -18°C to its melting point at 169.6°C. These phase transitions and the effects of the additives on these phase changes have been investigated. The phase transitions can be influenced by purity, thermal history, moisture content and crystallographical inhomogeneities as reported previously [1-9].

During the heating and cooling thermal cycle, AN experiences volume changes at phase transitions. Particularly at 32°C, crystal form IV changes to form III, which involves a volume change of 3.6% [7]. This expansion or contraction occurs in the temperature range of use of rocket motors or explosives. There have been failures of rocket motors, as a result of excessive pressure caused by cracks and excess burn surface resulting from the undesirable expansion and contraction. Much work has been done to overcome these difficulties. Some compounds such as NiO, CuO, ZnO, MgO, KNO_3, KF have been used in modifying the phase transition temperature [1-9]. Mishra reported that the addition of 10-17% by weight of potassium nitrate results in a large amount of residue in the combustion products and it tends to corrode and plug the rocket nozzle. A development patented by Mishra [10] provides solution to the above problems. The addition of 0.5 to 2% by weight of KF eliminated the undesirable volume changes in the temperature range of use of ammonium nitrate in rocket motor and explosives (-55°C to 80°C).

The thermal stability of ammonium nitrate has been extensively studied. It is a relatively stable compound which first decomposes and then explodes if heated while confined [11,12]. When ammonium nitrate is heated, it decomposes exothermically into nitrous oxide and water. At the same time, it dissociates endothermically into ammonia and nitric acid. As a result of these two concurrent reactions, the molten mass of nitrate

tends to reach a steady-state temperature, which is a function of ambient pressure and of the heating rate [13]. The thermal decomposition of fertilizer grade AN prills and AN in the presence of transition metals has also been examined by ARC [14-17].

A number of established thermal stability test techniques are widely used in evaluating hazards associated with runaway exothermic reactions. Micro-thermal techniques such as differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) use very small sample sizes which can introduce non-representative sampling problems with heterogeneous samples. Macro-thermal techniques, e.g. accelerating rate calorimetry (ARC) and the sensitive detector of exothermic process (SEDEX), tend to be used specifically for the detection of exothermic behaviour in considerably larger size samples. The ARC records lower initial temperatures for exothermic reactions due to heat accumulation effects [18]. Its limitation is that no quantitative data can be obtained for endotherm.

The Canadian Explosives Research Laboratory is equipped to evaluate thermal hazards of energetic materials. An accelerating rate calorimeter (ARC) has been used for evaluation of thermal hazards of materials associated with exothermic reactions. Differential scanning calorimetry (DSC) is an established analytical technique. Particularly it is useful to compensate for the weakness that the quantitative data of endotherms are not accessible by ARC. This report, part 1 of 2, describes the use of ARC to study the exothermic reaction of doped AN. Part 2 describes the influence of dopants on the phase transitions of AN and a discussion on the reactions occurring above the melting point under different degrees of confinement using DSC technique.

EXPERIMENTAL

Materials

Three doped ammonium nitrate samples were obtained from Defence Research Establishment Valcartier (DREV) and stored at room condition for

evaluation. A.C.S. grade ammonium nitrate stored in a desiccator was used for comparison. The samples are listed as follows:

1. Ammonium nitrate, A.C.S. grade, white crystal, obtained from Anachemia Chemicals Ltd.

2. Ammonium nitrate and KNO_3, DREV lot # TP-8619, beige coloured powder.

3. Ammonium nitrate and NiO, DREV lot # TP-8629, green coloured powder.

4. Ammonium nitrate and CuO, DREV lot # TP-8630, blue coloured powder.

Accelerating Rate Calorimetry (ARC)

Thermal decomposition of ammonium nitrate samples has been studied by ARC. This instrument was made by Columbia Scientific Industries in Austin, Texas. It was designed to maintain the sample in a near perfect adiabatic environment. Heat from the decomposition reaction is held in the reaction mass and the decomposition proceeds as a self-accelerating reaction. The theories and operation have been published [19,20] and will not be discussed in this paper.

All measurements were conducted using wide-mouth cylindrical Hastelloy C bombs weighing approximately 49 grams each. Six stainless steel screws secured a thin metal disk and a Teflon gasket to a flange on the bomb. Approximately 1 gram samples were accurately weighed into the sample container which resulted in a Ø value of about 12. Ø value is defined as:

$$\emptyset = 1 + \frac{C_v \text{ (bomb) } M\text{(bomb)}}{C_v \text{ (sample) } M \text{ (sample)}}$$

where C_v is the specific heat and M is the mass.

The step-heat method was employed in all the tests. First the sample and the bomb were heated to a start temperature of 100°C. Then the calorimeter was allowed to thermally stabilize for 30 minutes. Next came the search mode where the self-heat rate was monitored at a threshold detection limit of 0.02°C/min. The process of "heat-wait-search" was continued until a self-heat greater than 0.02°C/min was detected. After the detection of an exotherm, time and temperature data were collected until the end of the reaction.

RESULTS ANND DISCUSSION

The thermal stability of three samples, KNO_3 doped AN, NiO doped AN and CuO doped AN were examined by ARC. An A.C.S. grade ammonium nitrate crystal was used for comparison. Approximately 1.5 gram of A.C.S. grade ammonium nitrate was used for testing which resulted in a Ø value of 9. While 1 gram of the doped AN was used due to its reactivity.

For A.C.S. grade AN, an increase in the self-heat rate was detected at a temperature above 195°C. The first exotherm occurred and terminated after a short time. Taking the average of three repeated tests, the exotherm leading to ignition was detected at 218°C. Plots of self-heat rate as a function of 1/T are compared in Fig. 1 and the data are detailed in Table 1. Total weight loss after reaction was 98%.

When the KNO_3 doped AN was heated to 170°C (just above the melting point) and cooled, it separated into two layers with two different colours, white and beige. The first increase in self-heat rate occurred at 200°C and the onset temperature leading to ignition took place at 220-230°C with an average temperature of 225°C. In the early stages of decomposition, the reproducibility of the onset temperature was poor but the values became more consistent at a rate above 0.1°C/min as shown in Fig. 2. The amount of residue after reaction is approximately 14%.

TABLE 1
THERMAL DECOMPOSITION OF DOPED AMMONIUM NITRATE SAMPLES

RUN #	SAMPLE WT. (gm)	Ø	INITIAL DATA		AT 0.1 °C/min		AT 2 °C/min		AT MAX. RATE		Δ T_{AB} (°C)	WT. LOSS (%)	2 °C/min TO MAX RATE TIME (min)
			T_o (°C)	M_o (°C/min)	T (°C)	M (°C/min)	T (°C)	M (°C/min)	T_m (°C)	M_m (°C/min)			
AMMONIUM NITRATE (A.C.S. GRADE)													
200	1.5237	8.9	218.75	0.028	235.37	0.101	267.42	2.066	289.25	102.000	76.48	98.2	3.15
206	1.5058	9.0	215.46	0.022	233.08	0.107	262.54	2.050	286.73	112.666	75.45	98.1	3.24
379	1.5134	8.8	221.66	0.026	234.26	0.098	264.25	2.000	291.92	110.500	75.14	----	3.92
AN + KNO_3 (TP-8619)													
380	1.0406	12.7	231.57	0.029	241.60	0.103	261.27	2.033	290.98	107.714	60.43	87.3	3.16
384	1.0670	12.2	224.53	0.022	239.18	0.100	263.72	2.000	291.44	170.000	68.01	83.3	2.83
389	1.0130	12.8	219.33	0.030	236.95	0.100	261.37	2.105	279.18	105.000	67.82	87.6	3.01
AN + NiO (TP-8629)													
383	1.0370	13.1	232.72	0.024	246.75	0.104	272.28	1.935	294.14	59.500	65.10	91.5	3.13
386	1.0520	12.2	236.45	0.039	243.07	0.102	266.61	2.000	283.82	120.500	59.31	94.8	2.94
387	1.1135	11.9	236.07	0.024	238.68	0.108	267.15	1.909	294.74	47.500	61.44	95.1	3.73
AN + CuO (TP-8630)													
385	1.0160	12.2	221.97	0.047	233.99	0.102	259.52	2.105	290.04	126.666	68.07	93.5	3.32
388	1.0945	11.8	226.49	0.029	234.10	0.106	259.13	2.000	282.67	105.833	58.54	93.7	3.33
390	1.1068	11.8	226.40	0.031	235.42	0.107	265.56	1.937	287.79	117.500	68.06	93.7	3.53

For the NiO doped AN, an increase in the self-heat rate was detected at 220°C. The initial rate data of the major exotherm was found to average 235°C for the three tests (Fig. 3). Weight loss averaged 94%.

The third sample tested (CuO doped AN) indicated an increase in the self-heat rate at 215°C. Initial temperature for the major exothermic reaction was 225°C and the decomposition curves are shown in Fig. 4. Total weight loss was 94%.

After the melting point and before the exotherm leading to ignition, the doped AN samples showed instability with slow increase in self-heat rate as a general phenomenon. Usually the self-heat rate fluctuated at the region of detection limit and it varied slightly for each test. The reaction profile for the initial decomposition is complicated probably as a result of the properties of complex components in the doped AN.

All AN samples ignited with pressure built up and the cover disks were distorted after reaction. When the reaction rate is too fast, the thermocouple cannot accurately track the temperature. Therefore a temperature was determined at a self-heat rate of 2°C/min and it was defined as before ignition. The time from before ignition to maximum rate was about 3 minutes and it should raise some concern in hazard evaluation.

When the experimental results are interpreted, it is necessary to consider the type of test equipment and the experimental conditions employed. There are many factors that can affect the determined values. It includes sample size, method of heating, rate of heating and nature of sample. Hence, the application of these results should be considered carefully.

CONCLUSION

The onset decomposition temperature of NiO doped AN was detected at 235°C which is higher than the other two samples. However, when overall

decomposition patterns are compared, more variations are found for the NiO doped products. One advantage of the NiO doped AN over the KNO_3 doped product is the reduced amount of solid residue in the combustion products.

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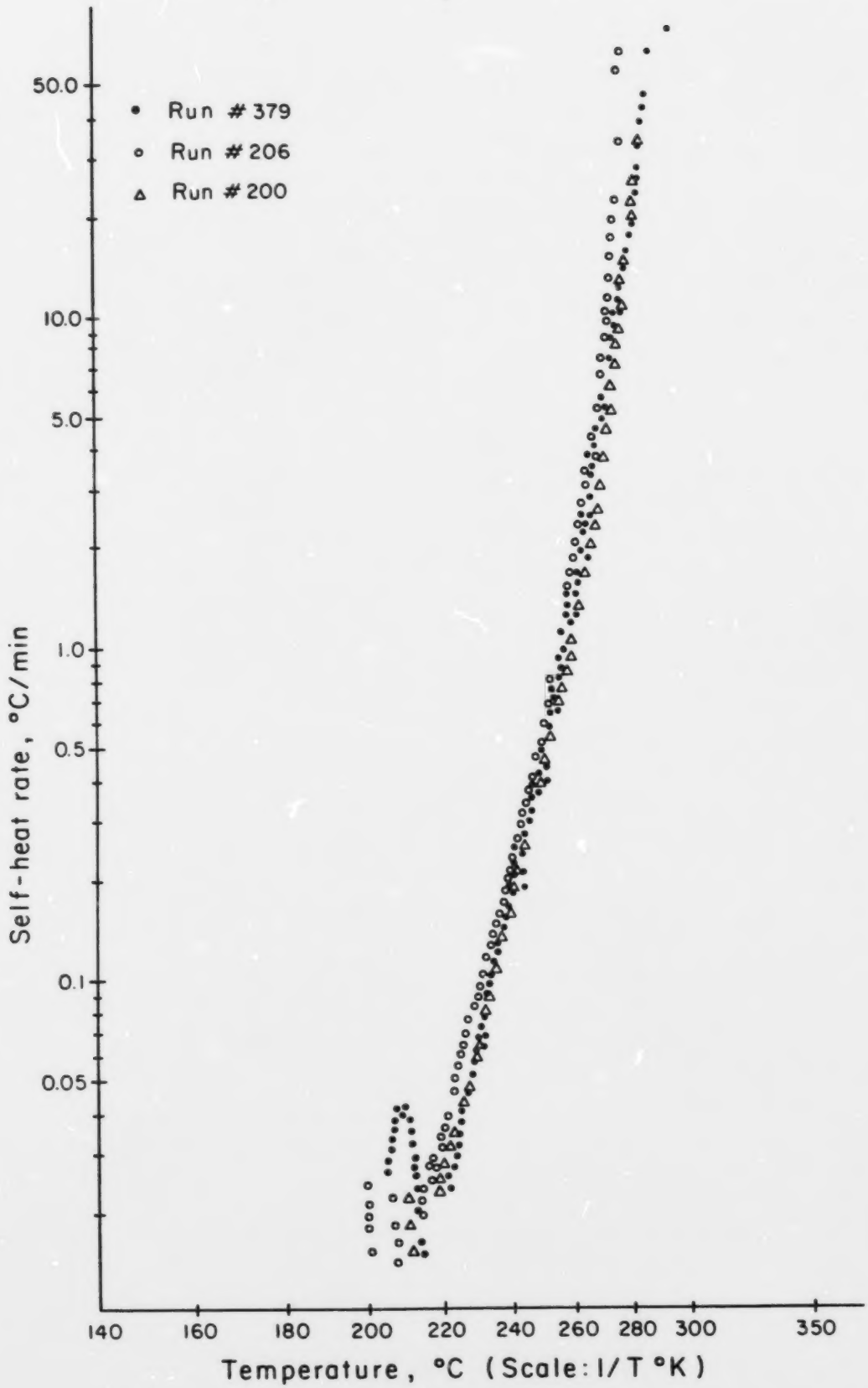

Fig. 1 - Thermal decomposition of ammonium nitrate.

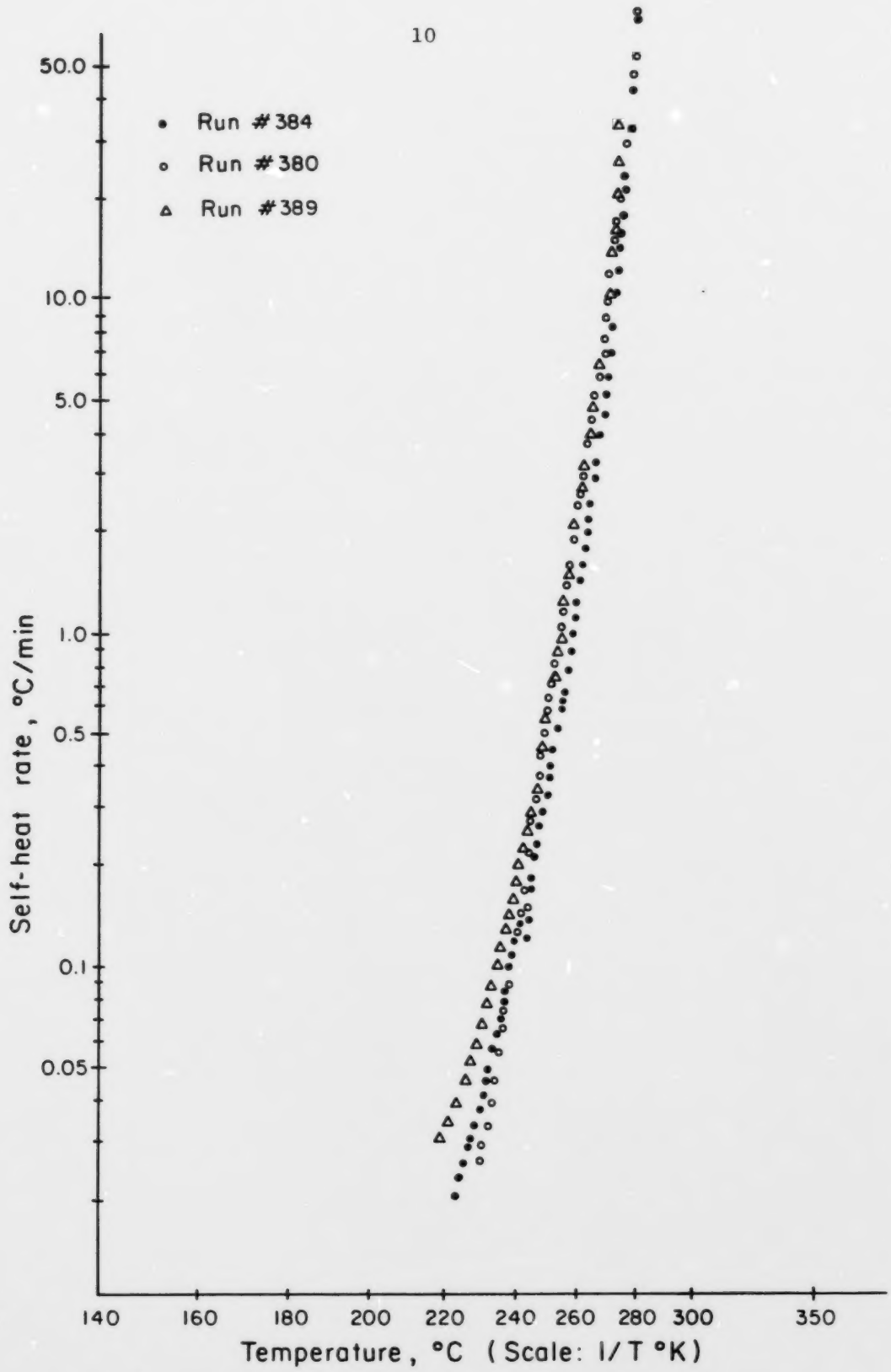

Fig. 2 - Thermal decomposition of KNO_3 doped ammonium nitrate.

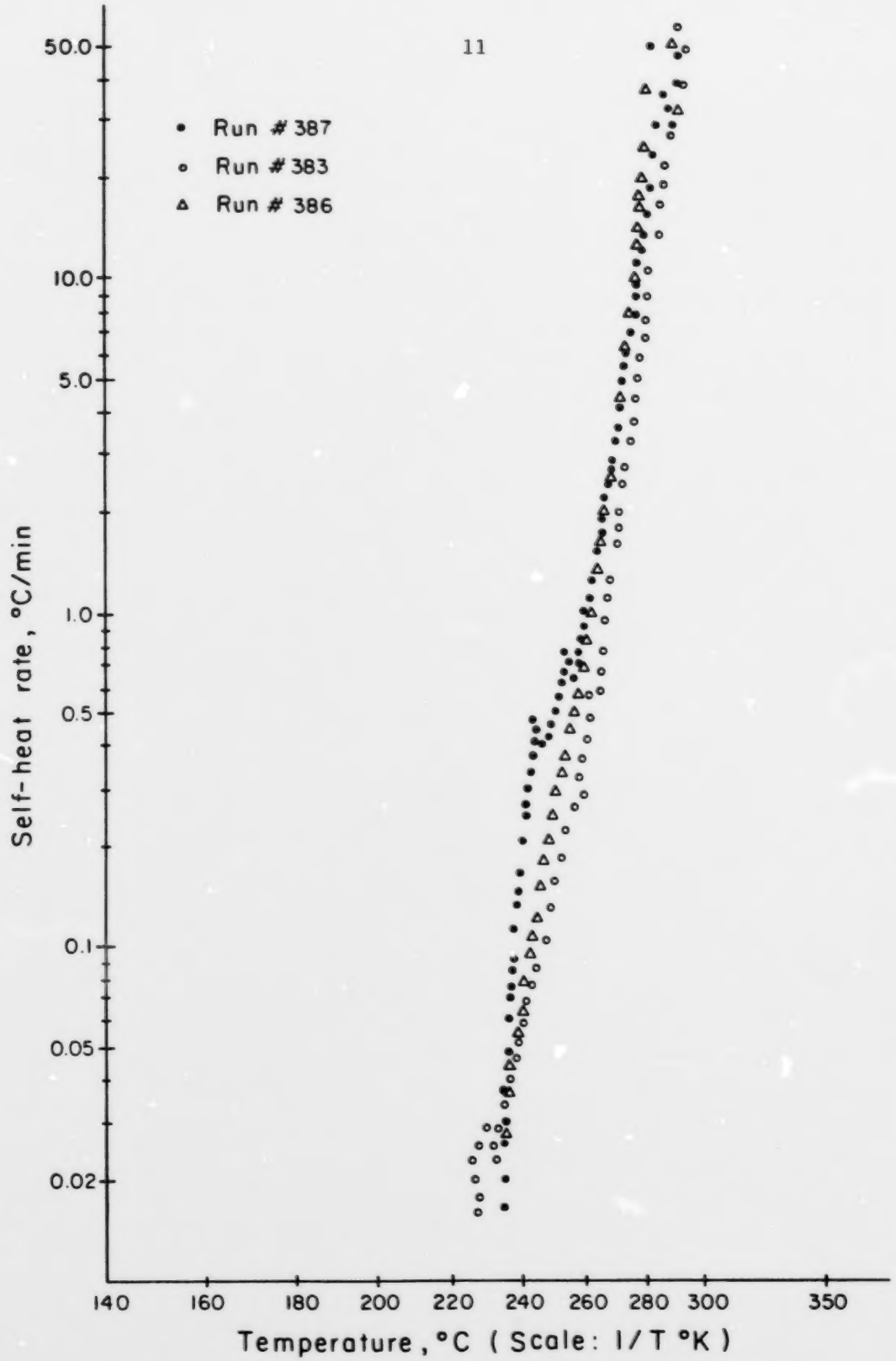

Fig. 3 - Thermal decomposition of NiO doped ammonium nitrate.

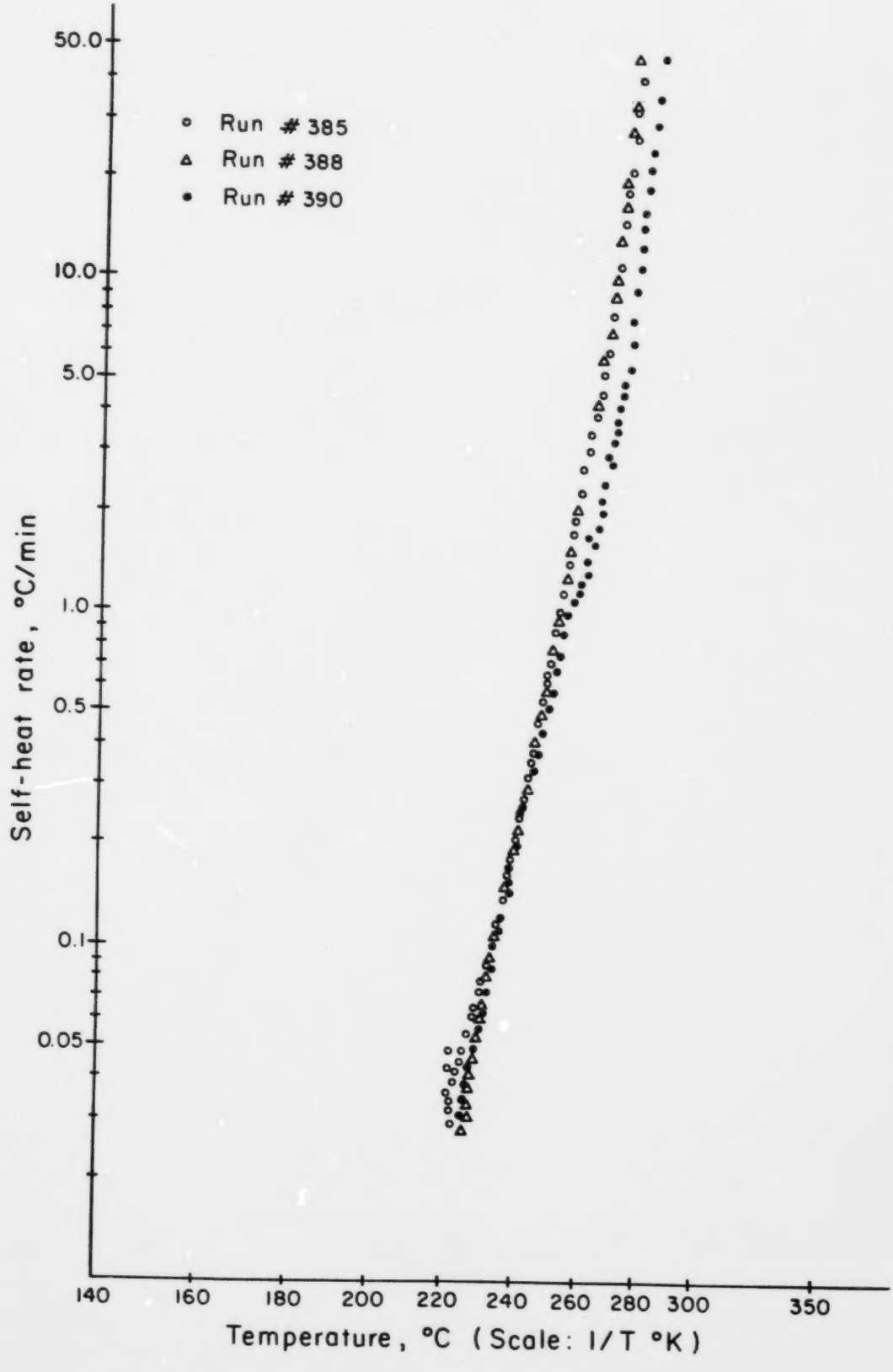

Fig. 4 - Thermal decomposition of CuO doped ammonium nitrate.